Short Time Quantum AC Response of a System of Nanomagnets

G. Rose[1] and P. C. E. Stamp[1,2]

[1] *Department of Physics and Astronomy, and Canadian Institute for Advanced Research, University of British Columbia, Vancouver B.C. V6T 1Z1 Canada*

[2] *Institut Laue-Langevin, Ave. des Martyrs, Grenoble 38042, France*

We calculate the magnetization relaxation in the short-time regime for an ensemble of nanomagnets in the presence of a low frequency external AC biasing field at temperatures lower than the magnetic anisotropy energy of the individual nanomagnets. It is found that the relaxation is strongly affected by AC fields with amplitude larger than that of the T_2 fluctuations in the nuclear field. This will allow experimental probing of the nuclear spin relaxation mechanism.

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1. INTRODUCTION

Recent experiments[1,2,3,4,5,6,7] on ensembles of magnetic macro-molecules have shown evidence for resonant tunneling relaxation. Two of these experiments show evidence of tunneling in the "quantum regime", where only the two lowest levels of each molecule are occupied; in the "Mn-12" molecule,[6] this happens below a crossover temperature $T_c \approx 2K$ and in the "Fe-8" molecule,[7] below $T_c \approx 0.4K$. Experiments in the Fe-8 system have gone down to 70 mK, with no change in the relaxation characteristics below 0.36 K; this constitutes *prima facie* evidence for a quantum regime in Fe-8 molecular crystals.[8,11] Theoretical work[8,9,12] on the "quantum relaxation" below T_c indicates that intermolecular dipole coupling and hyperfine coupling to the nuclear spins are necessary to explain the relaxation characteristics below T_c. A number of predictions based on this theory have recently been verified experimentally;[12,13] this work is discussed elsewhere in

this volume.[14] In particular, the prediction of a universal short-time "square root" relaxation has been verified, with a characteristic time τ_Q which depends on both dipolar and hyperfine interactions (as well as the tunneling matrix element Δ_0).

At present there is no direct measure of Δ_0 in these systems, making it hard to verify whether the observed τ_Q is that predicted by theory. In this paper we give preliminary results of a theory of quantum relaxation of ensembles of nanomagnets in the presence of an applied AC field. We show that the relaxation characteristics are strongly altered, in a way which should allow (i) the determination of Δ, and (ii) the demonstration that τ_Q is controlled by nuclear spins as well as by dipolar interactions.

We begin by considering an ensemble of nanomagnets or magnetic macromolecules. The high energy Hamiltonian for such systems has been shown to flow under reduction of temperature to a fixed point effective Hamiltonian given by

$$H = \sum_{\vec{r}} H^{(0)}(\vec{\tau}, \{\vec{\sigma}_k\}) + \sum_{\vec{r},\vec{r}'} H_D(\vec{\tau}_z^{\vec{r}}, \vec{\tau}_z^{\vec{r}'}) + \sum_{k,k'} V(\vec{\sigma}_k, \vec{\sigma}_{k'}) \qquad (1)$$

where $\vec{\tau}^{\vec{r}}$ is a Pauli matrix acting at molecular site $\vec{r}$, in the Hilbert space of the two lowest molecular states, and $\vec{\sigma}_k$ is a Pauli matrix acting on the two relevant states of the kth nuclear spin; we assume that $k = 1..N$. The internuclear term $V(\vec{\sigma}_k, \vec{\sigma}_{k'})$ is usually dipolar, and $|V_{k,k'}| \approx 1-100kHz$ (and measurable as T_2^{-1}, in for example nuclear spin echo experiments). Below T_c, H_D is diagonal in $\vec{\tau}_z$ (molecular flip-flop transitions are rare); it causes a bias $\xi_D(\vec{r}) = \sum_{\vec{r}} V_D(\vec{r} - \vec{r}')\vec{\tau}_z^{\vec{r}'}$ at site $\vec{r}$, which varies over a scale $E_D \approx 0.5K$ around the sample. In the absence of nuclear spins

$$H^{(0)}(\vec{\tau}^{\vec{r}}) = \Delta_0 \vec{\tau}_x^{\vec{r}} \qquad (2)$$

but in general one has[10]

$$H^{(0)}(\vec{\tau}^{\vec{r}}, \{\vec{\sigma}_k\}) = \Delta_0[\cos\{\Phi + \sum_{k=1}^N \alpha_k \vec{n}_k \bullet \vec{\sigma}_k\}\hat{\tau}_+ + H.C.]$$

$$+ \frac{\hat{\tau}_z}{2} \sum_{k=1}^N \omega_k^{||}\vec{l}_k \bullet \vec{\sigma}_k + \frac{1}{2} \sum_{k=1}^N \omega_k^{\perp}\vec{m}_k \bullet \vec{\sigma}_k \qquad (3)$$

This complex fixed point Hamiltonian contains all coupling effects between the molecular spin at $\vec{r}$ and the surrounding nuclear spins.[8,10] Of crucial importance are the diagonal hyperfine couplings $\omega_k^{||}$ to each $\vec{\sigma}_k$ (varying between $\approx 0.1mK - 0.5K$ in different systems), and the complex dimensionless amplitude α_k for $\vec{\sigma}_k$ to flip when $\vec{\tau}^{\vec{r}}$ does. $\vec{l}_k, \vec{m}_k$ and $\vec{n}_k$ are unit vectors,

and Φ is a renormalized Kramers-Berry-Haldane phase (given by $\Phi = \pi S$ when $\frac{1}{2}\sum_{k=1}^{N}|\alpha_k|^2 << 1$).

Typically, experiments begin by first polarizing the system, with all molecules aligned, and then watching the magnetization $M(t)$ decay with time t. Here we assume zero applied field, but add an AC field $H_{ac}(t) = \sum_{\vec{r}} A\cos(\omega t)\vec{\tau}_z^{\vec{r}}$. The question that we wish to now ask is this–in the experimentally relevant region $\frac{1}{2}\sum_{k=1}^{N}|\alpha_k|^2 << 1$, ie. where no nuclear spins flip during tunneling, what will the magnetization of the crystal look like at short times in the presence of this AC field?

2. THE GENERALIZED MASTER EQUATION

We may write the magnetization of our system in the form

$$M(t) = \sum_{\vec{r}} \int d\xi \, M(\vec{r}, \xi, t) = \sum_{\vec{r}} \int d\xi (2P_\uparrow(\vec{r}, \xi, t) - 1) \qquad (4)$$

where $P_\uparrow(\vec{r}, \xi, t)$ is the normalized probability of the central spin at site $\vec{r}$ to be "up" (ie. in state $|S_z = +S\rangle$) and in a static bias ξ at time t.

A solution for $P_\uparrow(\vec{r}, \xi, t)$ over timescales $\approx O(1/\omega)$ is rather messy. However experimentally one is usually interested in relaxation over much longer timescales, in which case one can write a kinetic or "master" equation of the form

$$\dot{P}_\alpha(\vec{r}, \xi, t) = -W(A, \omega; \xi)\{P_\alpha(\vec{r}, \xi, t) - P_{-\alpha}(\vec{r}, \xi, t)\}$$

$$-\sum_{\vec{r}',\alpha'} \int d\xi' W(A, \omega, \xi')[P_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}'; \xi, \xi'; t) - P_{\alpha\alpha'}^{(2)}(\vec{r}, \vec{r}'; \xi - \alpha\alpha' V_D(\vec{r} - \vec{r}'), \xi'; t)]$$

$$(5)$$

where $P^{(2)}$ is the usual 2-molecule distribution function. Note that we have assumed that nuclear T_2 fluctuations have decorrelated each pass of the local bias field through resonance from the others; this implies that $\omega < NT_2^{-1}$. When A or ω are zero, the master equation reduces to a "static" kinetic equation,[11] in which $W(A, \omega; \xi) \rightarrow \tau_N^{-1}(\xi) \sim (\Delta^2/\xi_0)e^{-|\xi|/\xi_0}$, the nuclear spin driven transition rate.[8,11] We ignore higher order multimolecular terms $P^{(3)}, P^{(4)}$, etc. and assume approximate factorization of $P^{(2)}$. As before,[11] this means that the results we derive are only valid when $1 - M(t)/M_0 << 1$, where M_0 is the saturation magnetization.

Our method generalizes that given for a static applied field; we first solve for the rate function $W(A, \omega; \xi)$ for a single molecule,[8] but now in an AC field, so that the total longitudinal field acting on $\vec{\tau}_x^{\vec{r}}$ is

$$\xi_{tot}^{\vec{r}} = \xi(\vec{r}) + A\cos(\omega t) + \delta\xi_{\vec{r}}(t) \qquad (6)$$

in which $\delta\xi_{\vec{r}}(t)$ is the rapidly varying component coming from T_2 fluctuations, and $\xi(\vec{r}) = \xi_D(\vec{r}) + \xi_N(\vec{r})$ is the slowly varying sum of dipolar fields and longitudinal hyperfine fields ($\xi_N(\vec{r}) = \omega_0 M_{\vec{r}}$ for a system with a single hyperfine coupling ω_0 and total nuclear polarization $M_{\vec{r}} = \sum_{k=1}^{N} < \vec{\sigma}_k^z >$ along the molecular easy axis).

In what follows we assume (as noted above) that no nuclear spins flip during tunneling–the general results including nuclear flips will be published elsewhere. We also assume that the nuclear spins are in a thermal ensemble with $kT >> \omega_0$ (it is easy to show that the AC field will drive them into such a high-T distribution; and all experiments so far have $kT >> \omega_0$ anyway).

In present experiments on magnetic macromolecules where the molecular spin $S \approx O(10)$, an AC field of amplitude $\delta H = A/g\mu_B S$ equal to 1 G is equivalent to a bias amplitude $A \approx 50MHz \approx 25mK$. Experiments can range roughly between $10^{-5}G < \delta H < 100G$ (depending on ω). Thus we will assume that $\Delta\xi > A >> \Delta$, where $\Delta\xi \approx 0.5 - 1K$ is the total spread in ξ caused by dipolar and hyperfine fields; however the ratio A/ξ_0 is arbitrary. We then find the following results.

(i) $A/\xi_0 >> 1$ (large AC amplitude). The transition rate $W(A, \omega; \xi) \approx W_0(\xi/A)\Theta(A^2 - \xi^2)$, where

$$W_0(\xi/A) = \frac{\Delta^2}{\sqrt{A^2 - \xi^2}} \tag{7}$$

for $A - |\xi| >> \xi_0^2/2A$ and

$$W_0(\xi/A) = \frac{\Delta^2}{\xi_0} \tag{8}$$

for $A - |\xi| < \xi_0^2/2A$.

(ii) $A/\xi_0 < 1$ (small AC amplitude). In this regime the dynamics are controlled by the nuclear T_2 field; one gets, for the transition rate,

$$W(A, \omega; \xi) \approx \frac{\Delta^2}{\xi_0} e^{-|\xi|/\xi_0} \tag{9}$$

The essential effect of the AC field, when $A >> \xi_0$, is to spread the resonant tunneling over a much larger energy range $2A$ (but at a reduced rate, except when $|\xi| \approx A$, and the AC field itself varies slowly, so that $\dot{\xi}(t)$ is dominated by T_2 fluctuations). As the amplitude of the AC field is decreased the dynamics become completely dominated by nuclear T_2 effects with the crossover occuring at $A \approx \xi_0$.

3. SHORT TIME DYNAMICS

The solution for $M(t)$ is now straightforward, following our previous methods.[11] For large AC amplitude one gets

$$\dot{M}(t) = -\frac{2M(t)}{\pi} \int_{-A}^{A} d\xi \frac{\Gamma(t)}{[\xi - E(t)]^2 + \Gamma^2(t)} W_0(\xi/A) \qquad (10)$$

for an ellipsoidal sample, where the internal field has Lorentzian spread $\Gamma(t) = \frac{4\pi^2 E_D}{3^{5/2}}(1 - M(t))$ and mean $E(t) = cE_D(1 - M(t))$, and c depends on the specific geometry of our ellipsoid. For small AC amplitude one gets the square root relaxation found previously.[11]

The solution to the large AC amplitude problem (10) is clearly not square root at short times; in fact one gets

$$1 - \bar{M}(t) \approx e^{-t/\tau_{ac}} \qquad (\ 1 - \bar{M}(t) << A/E_D \ ) \qquad (11)$$

where $\bar{M}(t) = M(t)/M_0$; the rate $\tau_{ac}^{-1} \approx \Delta^2/A$, which is a factor E_D/A faster than the relaxation "rate" $\tau_Q^{-1} \approx \Delta^2/E_D$ which one obtains for an ellipsoid in the square root regime.[11] At longer times, once the internal field $E(t) >> A$, we get

$$1 - \bar{M}(t) \approx \sqrt{t/\tau_Q} \qquad (\ 1 - \bar{M}(t) >> A/E_D \ ) \qquad (12)$$

Clearly if A/E_D is not too small, we may never see a clear square root relaxation; correlations in $P^{(2)}$ will emerge before the square root does.

For a non-ellipsoidal sample we find in general that the exponential relaxation rate will become $(\tau_{ac}^{inhom})^{-1} \approx \Delta^2/E_D \equiv (A/E_D)\tau_{ac}^{-1}$, since the internal fields are now spread over a large range $\approx E_D$ in bias space. In all but specially-shaped samples, this will be what is observed.

It is clear from these results that AC experiments can test the nuclear spin mediated tunneling mechanism, since the prediction here is that it is only when $A > \xi_0$ that significant deviations from the static square root relaxation will appear. This prediction is quite different from what one would find if we assumed that tunneling proceeded at a rate Δ for molecules near exact resonance ($|\xi| < \Delta$); in this case the square root relaxation would break down for $A > \Delta$. Since in the Mn-12 and Fe-8 systems, $\Delta \approx 10^{-10} - 10^{-9}K$, this would imply a breakdown of the square root law once A exceeded roughly $10^{-8} - 10^{-7}G$, a very small value indeed!

Notice also that since $\tau_{ac}^{-1} \approx \Delta^2/A$, we have a way of determining the important parameter Δ directly in experiments, knowing A. It is clear that the results of AC experiments conducted near $H = 0$ in magnetic macromolecular crystals will give a crucial test of present theory.

G. Rose and P.C.E. Stamp

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REFERENCES

1. C. Paulsen and J.G. Park, in *"Quantum Tunneling of Magnetization- QTM'94"* (ed. L. Gunther and B. Barbara), Kluwer publishing, pp. 189- 207 (1995).
2. M. Novak and R. Sessoli, pp. 171-188, *ibid.*
3. D.D. Awschalom *et.al.*, Science **258**, 414 (1992) and refs. therein.
4. B. Barbara *et.al.*, J. Mag. Magn. Mat. **140-144**, 1825 (1995).
5. J.R. Friedman *et.al.*, Phys. Rev. Lett., **76**, 3830-3833 (1996).
6. L. Thomas *et.al.*, Nature **383**, 145-147 (1996).
7. C. Sangregorio *et.al.*, Phys. Rev. Lett., **78**, 4645 (1997).
8. N.V. Prokof'ev and P.C.E. Stamp, J. Low Temp. Phys. **104**, 143 (1996).
9. P.C.E. Stamp, pp. 101-197 in *"Quantum Tunneling in Complex Systems"*, ed. S. Tomsovic (World Scientific, 1998).
10. I. Tupitsyn, N.V. Prokof'ev, P.C.E. Stamp, Int. J. Mod. Phys. **B11**, 2901 (1997).
11. N.V. Prokof'ev and P.C.E. Stamp, Phys. Rev. Lett. (in press); cond-mat 9710246.
12. T. Ohm, C. Paulsen, preprint (Dec. 20, 1997); and see this volume.
13. L. Thomas, B. Barbara, preprint (Jan 16, 1998); and see this volume.
14. N.V. Prokof'ev and P.C.E. Stamp, this volume.